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THE PHILIPPINE
JOURNAL OF SCIENCE

ALVIN J. COX, M. A., PH. D.
GENERAL EDITOR

SECTION A
CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF
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T. DAR JUAN, A. B., PHAR. D.; A. H. WELLS, A. B.
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A TEN-YEAR INDEX

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A, CHEMICAL AND GEOLOGICAL SCIENCES
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VOL. XIII JANUARY, 1918 No. 1

WATER ANALYSIS IN THE FIELD[1]

By GEORGE W. HEISE and A. S. BEHRMAN

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila)

ONE PLATE

Recent developments in water analysis have emphasized the importance of making examinations at the source whenever possible. The work of the Bureau of Science has shown the need of field investigations and the peculiar applicability of field methods to Philippine conditions. Accordingly field work has been made one of the most important features of our study of water supplies.

Owing to the comparative isolation of the Philippines, the great distance from scientific or manufacturing centers, and the consequent loss of time when apparatus and supplies are procured from abroad, we have found it necessary, to a large extent, to build our own apparatus, to prepare our own reagents for field use, and to devise and adapt methods suitable to our needs.

The field work of the Bureau of Science has been carried on for three years. Because of the importance of field methods at the present time, and because workers in as isolated places as the Philippines will continue to be dependent, in a great measure, on their own resources, we have thought it advisable to describe our field methods and apparatus in detail.

Our methods are based upon those described by Leighton.[2] Several changes, however, have been made. A "tabloid" de-

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[1] Received for publication August, 1917.

[2] Leighton, M. O., Field assay of water, *U. S. Geol. Surv., Water Supply Paper* (1905), No. 151.

termination of acidity and a rough estimate of the total amount of solid matter have been added, the soap method for total hardness has been replaced by a new and more accurate procedure, and several minor modifications in the details of manipulation of some of the old methods have been introduced. Other minor changes have been made in apparatus, as will become evident in the detailed description to follow.

In connection with the study of potable waters, a field bacteriological examination is also made. This consists in 24- and 48-hour colony counts at ordinary temperature and a presumptive test for *Bacillus coli* or related organisms that would indicate fæcal contamination. The uniform tropical temperature (25° to 30° C.) makes this bacteriological work a very simple, while a very valuable, feature of the examination.

The outfit has been gradually reduced in size, although the number of determinations made has been increased; so now enough apparatus and materials for a month's chemical work can be carried in an army telescope. This makes a package weighing less than 20 kilograms, which fits well on one side of a packsaddle or on the back of a cargador. The bacteriological outfit is carried in a small metal box. The complete equipment is shown in Plate I.

A comprehensive sanitary survey, embracing, in so far as possible, all those features that might influence the quality of the water under examination, is, of course, included in field work.

The details of the methods employed in regular field examination are outlined and briefly discussed.

TABLE I.—*Chemical methods.*

Quantitative.	Qualitative.
Color	Odor
Turbidity (as SiO_2)	Total solids
Alkalinity (as $CaCO_3$)	Appearance on ignition
Acidity (as CO^2)	Calcium
Iron (Fe)	Classification for boiler use
Chlorides (Cl)	
Normal carbonates (as Na_2CO_3)	
Bicarbonates (as $CaCO_3$ or HCO_3) [by calculation]	
Sulphates (as SO_3)	
Total hardness (as $CaCO_3$)	
Estimated encrustants [by calculation]	

Color is determined with the United States Geological Survey color outfit described by Leighton,[3] consisting of a standard length aluminium tube, which is filled with the water under examination. The color of this column of water, viewed longitudinally, is matched by disks of colored glass that have been rated in parts per million to correspond to the platinum-cobalt standard.

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[3] Op. cit.

Iron is conveniently determined with the same outfit as used for color, as described by Leighton. The only extra equipment required is a series of prepared colored disks corresponding to those produced by treating standard solutions of iron. These disks have not been available. In lieu thereof, red and yellow glasses from the Lovibond tintometer have been employed, in connection with two matched Nessler tubes in galvanized iron outer tubes. When 100 cubic centimeters of water were used in a determination, it was found that a summation of 6.0 on the Lovibond scale was very nearly equal to 1 part per million of iron (as Fe). The following is the procedure employed:

To 100 cubic centimeters of the water under examination in a Nessler tube add 4 cubic centimeters of concentrated nitric acid. Mix thoroughly by pouring six or seven times from one tube to another and allow to stand at least five minutes to insure complete oxidation. Then add 6 cubic centimeters of a 2 per cent solution of potassium sulphocyanide, mix thoroughly by several pourings, and allow to stand ten minutes for the color to develop. Exactly at the end of ten minutes make the color comparison with the Lovibond glasses under the empty Nessler tube, using a piece of white paper to reflect the light. Hold the tubes with one hand sufficiently high to reflect all the light possible. Interchange the tubes several times to avoid inequalities of light. The tubes should be held in such a position that both may be seen with one eye. Obviously, the final reading may be made either by using all the glasses under the empty Nessler tube or with some under the water as well. In this way intermediate values sometimes not otherwise obtainable may be found.

In all cases the nitric acid used should be tested beforehand for iron, this being a not infrequent impurity.

Turbidity is determined with the electric turbidimeter described in Leighton's paper. By means of an electric flash light, a cross of light is provided at the bottom of a long graduated tube. The well-shaken, turbid water is poured in until the sharp image has disappeared and the hazy cross of light just disappears. This is taken as the end point in the lower part of the tube. In the upper part of the tube (that is, for slightly turbid liquids) there is no hazy cross of light, and the end point is taken as the depth at which the sharp image of the cross disappears, giving place to a slightly blurred one—that is, it seems out of focus. Table II is provided for converting the turbidimeter depths to parts per million of silica.

TABLE II.—*Conversion of turbidimeter readings in depth to parts per million of turbidity.*

Reading.	Turbidity (as SiO_2).	Reading.	Turbidity (as SiO_2).	Reading.	Turbidity (as SiO_2).	Reading.	Turbidity (as SiO_2).
cm.	*Parts per million.*	*cm.*	*Parts per million.*	*cm.*	*Parts per million.*	*cm.*	*Parts per million.*
2.3	1,000	6.3	350	10.5	210	19.6	110
2.6	900	7.3	300	11.0	200	21.7	100
2.9	800	7.6	290	11.5	190	23.0	90
3.2	700	7.8	280	12.1	180	25.0	80
3.5	650	8.1	270	12.8	170	28.0	70
3.8	600	8.5	260	13.6	160	31.0	60
4.1	550	8.7	250	14.4	150	35.0	50
4.5	500	9.1	240	15.4	140	42.0	40
4.9	450	9.5	230	16.6	130	52.0	30
5.6	400	10.0	220	18.0	120	70.0	20

Turbidity may be also determined with the turbidity rod, which consists merely of a bright platinum wire fastened at right angles to a tape. Under the proper conditions the tape is lowered into the water under examination, and the end point is taken as the depth at which the wire just disappears from view. The tape is calibrated directly to read parts per million of silica (SiO_2).

The disadvantage of the turbidity-rod method is the required nicety of adjustment of conditions, involving the use of a large sample under circumstances often impossible. The turbidimeter method, on the contrary, is independent of most of these conditions. Only a small sample is required. Since the method is based on the diffraction of light, the accuracy of the determination is almost independent of the intensity of the light and, therefore, of the condition of the batteries and bulb. It follows directly that the original calibration as given by Leighton is applicable to any well-constructed turbidimeter. No difficulty was experienced in having a suitable instrument constructed for our purposes.

Sulphates are also determined with the turbidimeter, as described by Leighton. To 100 cubic centimeters of the water is added 1 cubic centimeter of hydrochloric acid (50 per cent concentrated acid by volume) and 1 gram of powdered crystals of solid barium chloride. Precipitations are conveniently made in 250 cubic centimeter glass-stoppered bottles. The water is allowed to stand for ten minutes, with frequent shakings. The turbidity produced is then determined with the turbidimeter as before. The sulphate content (as parts per million of SO_3) is read from Table III.

TABLE III.—*Converting readings in depths by the turbidimeter into parts per million of sulphate.*

Reading in centimeters.	Parts per million (as SO_3).	Reading in centimeters.	Parts per million (as SO_3).	Reading in centimeters.	Parts per million (as SO_3).
1.0	522	5.4	104	10.8	53
1.1	478	5.5	103	11.0	52
1.2	442	5.6	101	11.2	51
1.3	410	5.7	99	11.4	50
1.4	383	5.8	97	11.6	49
1.5	359	5.9	96	11.8	48
1.6	338	6.0	94	12.0	47
1.7	319	6.1	93	12.4	46
1.8	302	6.2	91	12.6	45
1.9	287	6.3	90	12.8	44
2.0	273	6.4	88	13.0	43
2.1	261	6.5	87	13.5	42
2.2	250	6.6	86	14.0	41
2.3	239	6.7	84	14.5	39
2.4	230	6.8	83	15.0	38
2.5	221	6.9	82	15.5	37
2.6	213	7.0	81	16.0	36
2.7	205	7.1	80	16.5	35
2.8	198	7.2	79	17.0	34
2.9	191	7.3	78	17.5	33
3.0	185	7.4	77	18.0	32
3.1	179	7.5	76	18.5	31
3.2	173	7.6	75	19.0	30
3.3	168	7.7	74	20.0	29
3.4	164	7.8	73	21.0	28
3.5	159	7.9	72	22.0	27
3.6	155	8.0	71	22.5	26
3.7	151	8.1	70	23.0	25
3.8	147	8.2	69	24.0	24
3.9	144	8.3	68	25.0	23
4.0	140	8.5	67	26.5	22
4.1	137	8.6	66	28.0	21
4.2	133	8.7	65	29.0	20
4.3	131	8.8	64	31.0	19
4.4	128	9.0	63	33.0	18
4.5	125	9.1	62	35.0	17
4.6	122	9.3	61	37.5	16
4.7	119	9.5	60	40.0	15
4.8	117	9.7	59	43.0	14
4.9	115	9.8	58	26.5	13
5.0	113	10.0	57	50.0	12
5.1	110	10.2	56	55.5	11
5.2	108	10.4	55	62.0	10
5.3	106	10.6	54	68.0	9

Calcium was formerly determined turbidimetrically by the United States Geological Survey method, but this has been abandoned because of its inaccuracy.

The qualitative field test for calcium is made by adding enough ammonia to some of the water in a test tube or bottle to make it alkaline to litmus and adding some ammonium oxalate.

Total solids are determined qualitatively by evaporating 50 cubic centimeters of the water in a porcelain casserole to dryness over an alcohol lamp. The solid content is reported merely as "very small," "moderate," "large," etc. The residue is then ignited, and any change in "appearance on ignition" is noted. This may be a browning or blackening due to organic matter, or a deep red-brown coloration due to the oxidation of considerable amounts of iron present. The last is of value as a confirmatory test for large amounts of iron.

Odor is reported, wherever possible, in such a way that both the derivation and the relative amount are indicated, for instance, "very slightly sulphuretted," "strongly acid."

Alkalinity, acidity, chlorides, normal carbonates, and total hardness are determined by the use of tablets, as outlined by Leighton. In brief, this method consists of the use of pellets containing known amounts of reagents, instead of standard solutions. The titrations are performed in a small (100 to 150 cubic centimeters), heavily glazed porcelain mortar, a pestle being used to crush the pellets and to stir the liquid. The volume of water used for a titration is conveniently measured from a tall, 100 cubic centimeter graduated cylinder, provided with a double scale, so that both the water withdrawn and the volume remaining can be directly read. What are practically duplicate determinations can be made very rapidly in the following manner:

A few pellets are crushed in the mortar, and water is added from the cylinder till the end point is reached. The volume used is noted. Several more pellets—preferably the same number as before—are added, followed by water from the cylinder, until the second end point is obtained. In this way not only is it possible to secure more accurate results by taking the mean of the two values obtained than by making a single determination, but in addition any gross error that may arise from an unclean mortar, contaminated indicator, or defective tablet can be detected and corrected.

The following reagents are used in tablets in the various determinations:

Sodium acid sulphate for alkalinity and normal carbonates;

sodium carbonate for acidity; silver nitrate for chlorides; and potassium palmitate for total hardness.

Kaolin is used as the filter and binding material for the sodium carbonate and silver nitrate pellets, while glucose is employed for those of sodium acid sulphate and potassium palmitate. Glucose is superior to kaolin, as it is completely soluble and consequently does not obscure the end point. It cannot, however, be used in the first two cases, because unstable pellets result. Water is used in all cases in making up the pill mass. The reagent is dissolved in water and carefully stirred into the binding material. The mass is kneaded in a mortar, more water being added if necessary, until it is homogeneous and of the desired consistency.

The tablets are made in a tablet mold. We use a hard rubber mold (No. 10, Whitall Tatum Company, for making 50 one-grain tablets at a time). The molded pellets are dusted with powdered talc, dried in the air and then in a desiccator over calcium chloride, after which they are packed in glass tubes, about 15 centimeters in length and holding about forty pellets each. The tubes are sealed with paraffin, and those containing pellets of silver nitrate are covered with heavy black paper. Needless to say, the silver nitrate pellets are made in a dark room.

The silver nitrate and sodium carbonate pellets retain their strength almost indefinitely without change. Those of sodium acid sulphate lose strength very slowly and should be restandardized every month. The potassium palmitate pellets lose strength rather rapidly and should be restandardized weekly.

Alkalinity.—Pellets are molded from a pill mass containing 6.5 grams of crystallized sodium bisulphate and 150 grams of glucose, the proportions that will yield a pill of very nearly the desired strength (one pellet equivalent to 1 milligram calcium carbonate, $CaCO_3$). The pellets are standardized by crushing five of them in a mortar with a little distilled water and adding a drop of butter yellow indicator solution (0.2 gram butter yellow in 100 cubic centimeters of alcohol). Tenth-normal sodium hydroxide or sodium carbonate is added till the end point is reached. From this titration the reacting value of the pellets may be readily calculated.

The field determination of alkalinity is analogous to the standardization of the pellets. The 100 cubic centimeter cylinder is filled to the mark with the water under examination. Two or three of the pellets are crushed in the mortar with a little of the water, and a drop of the indicator is added, followed by more water from the cylinder till the end point is reached.

The volume of water used in the titration is noted, readings being taken to the tenth of a cubic centimeter. Two or three more pellets are added, followed by more of the water to the second end point.

The alkalinity, expressed as parts per million $CaCO_3$, is readily calculated from the number and strength of pellets and the volume of water used in the determination. Thus, if 4 pellets of sodium bisulphate, each equivalent to 1.10 milligrams of calcium carbonate, require 22.4 cubic centimeters of the water for interaction, the alkalinity will be

$$\frac{1,000 \times 4 \times 1.10}{22.4} = 196$$

and would be reported as 200 (that is, in terms of two significant figures).

Normal carbonates.—If normal carbonates (or hydroxides) are present, the water will give a pink coloration with phenolphthalein. In this event the amount of normal carbonates is determined with pellets of sodium bisulphate. The procedure is identical with that for the determination of alkalinity, except that 5 drops of phenolphthalein indicator solution (1 per cent alcoholic) are used instead of the 1 drop of butter yellow. Where the normal carbonates are present only in small amount, half, or even a quarter, of a pellet may be all that can be used.

As phenolphthalein is sensitive to carbonic acid, the end point in this determination is reached when only half of the alkali is neutralized. Accordingly the same sodium bisulphate pellet that was equivalent to 1.10 milligrams of calcium carbonate in the determination of alkalinity will be equivalent to twice that amount, or 2.20 milligrams, when used in the determination of normal carbonates.

Thus, if 2 of these pellets required 57 cubic centimeters of the water for the reaction, the results expressed in parts per million of calcium carbonate would be

$$\frac{1,000 \times 2 \times 2.20}{57} = 77.$$

When, as is usually the case with Philippine waters, the phenolphthalein alkalinity is less than half that determined with butter yellow, the alkalinity of a natural water is caused by bicarbonates and normal carbonates and is equal to their sum. If, therefore, no normal carbonate is present, the alkalinity is numerically equal to the bicarbonates, when both are expressed in terms of calcium carbonate. If, when normal carbonates are present, the alkalinity is found to be equal to the normal carbonates—that is, when the phenolphthalein titration is one half that with butter yellow—the absence of bicarbonates is indicated. If the alkalinity is found greater than the normal carbonates, the difference will be bicarbonates, all expressed as calcium carbonate.

If, however, the phenolphthalein titration is more than one half that with butter yellow, the waters contain calcium or other alkaline hydrates (caustic alkalinity). In case the phenolphthalein and butter yellow titrations are identical, all of the alkalinity is due to hydrates.

The relations between the various forms of alkalinity just discussed are shown in Table IV.[4]

TABLE IV.—*Relation between normal carbonates, bicarbonates, and hydrates in natural waters, as indicated by titration with sulphuric acid (sodium bisulphate) in cold.*

	Carbonates.	Bicarbonates.	Hydrates.
$P=0$	0	B	0
$P<\frac{1}{2}B$	2P	B-2P	0
$P=\frac{1}{2}B$	2P	0	0
$P>\frac{1}{2}B$	2(B-P)	0	2P-B
$P=B$	0	0	B

P, phenolphthalein titration; B, butter-yellow titration.

When it is desired to express normal carbonates as sodium carbonate, the calcium carbonate value is multiplied by 1.06. Similarly the bicarbonates may be expressed as HCO_3 by multiplying the calcium carbonate equivalent by 1.22.

Acidity.—If a water reacts acid to phenolphthalein, the presence of carbonic or a mineral acid is indicated. In the first case bicarbonates may be present, but normal carbonates will not. In the second case neither bicarbonates nor normal carbonates can be present, and the water will react acid to butter yellow or methyl orange as well as to phenolphthalein.

Mineral acidity, when present, is determined with pellets of sodium carbonate, using butter yellow as an indicator. Total acidity, due to the combined effect of mineral and carbonic acids, is also determined with pellets of sodium carbonate, but in the presence of phenolphthalein as indicator. The carbonic acid acidity is the difference between the total and the mineral acidities.

Mineral acidity in natural waters is rarely encountered in the Philippines. Acidity is practically always due to free carbon dioxide and is, therefore, determined with sodium carbonate pellets, using 5 to 10 drops of phenolphthalein solution as indicator. The manipulation is identical with that described for "alkalinity" and "normal carbonates," except that, ordinarily, only one or two tablets, or even less, will be required for a titration. Furthermore, since the kaolin in the pellets slightly obscures the end point, the discrepancy between duplicate determinations is usually 0.5 cubic centimeter and often 1 cubic centimeter.

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[4] Cf. Standard Methods of Water Analysis, American Public Health Association, Boston. 2d ed. (1915), 39.

In the manufacture of the sodium carbonate pellets 4.0 grams of anhydrous sodium carbonate are used to 130 grams of kaolin. This gives a pellet of approximately the desired reacting value, namely, 1 milligram of carbon dioxide. To standardize, 5 of these pellets are triturated in a mortar with recently boiled distilled water, 5 drops of phenolphthalein solution are added, and the solution is titrated with 0.1 N sulphuric acid.

If, in a field determination, it is found that the average of two readings taken for the reaction with 1 pellet equivalent to 0.95 milligram of carbon dioxide (phenolphthalein being used as indicator) is 24 cubic centimeters of the water, the acidity, expressed in parts per million of carbon dioxide, would equal

$$\frac{1,000 \times 0.95}{24} = 40.$$

Chlorides.—For the determination of chlorides, "weak" and "strong" pellets of silver nitrate are employed. The former are each equivalent to about 1 milligram of chlorine, the latter to 10 milligrams. In the manufacture of the weak pellets, 12.5 grams of silver nitrate and 200 grams of kaolin are used, while 156 grams of silver nitrate and 250 grams of kaolin are the proportions used for the strong pellets.

The pellets are standardized with a sodium chloride solution, which is conveniently made to be equivalent to 1 milligram of chlorine per cubic centimeter. Potassium chromate is used as an indicator.

The determination of chlorides in the field is rapid and simple. A small quantity of water, usually only 10 or 15 cubic centimeters, is introduced from the filled 100 cubic centimeter graduate into the mortar. Five drops of potassium chromate solution (5 per cent) are added as indicator. If the chlorine content of the water is high, "strong" silver nitrate pellets are added one at a time, with thorough mixing, until an excess is indicated by the rose color of silver chromate. If the chlorine content is low, "weak" pellets are added till the end point is passed. If the chlorine content is low, that is, under 10 parts per million, a half or even quarter tablet will be sufficient. In any case, after an excess of silver nitrate has been provided, more water is added from the cylinder until the rose color is entirely displaced by a bright yellow, corresponding to the shade used in standardization. Check determinations may be made as before by adding more pellets and titrating.

If, to react with a half of a "weak" tablet (a whole tablet being equivalent to 0.96 milligram of chlorine), there were required 76 cubic centimeters of the water under examination, the chlorine content, expressed in parts per million of chlorine, would be found from the expression

$$Cl = \frac{1,000 \times 0.5 \times 0.96}{76} = 6.3.$$

Total hardness.—The pellets of potassium palmitate used for the determination of hardness are made from a pill mass of glucose and potassium palmitate. One hundred grams of glucose are used with an amount of potassium palmitate corresponding to 15 grams of palmitic acid. To make potassium palmitate, palmitic acid is dissolved in alcohol and neutralized with normal alcoholic potash solution, using phenolphthalein as indicator. The resulting alcoholic solution is then evaporated to dryness. The residue may be used without further treatment for making the pellets.

The following method is employed for the standardization of the pellets: A saturated solution of calcium hydroxide is prepared from pure calcium oxide. The normality of this is determined by titration of 25 cubic centimeters with 0.1 *N* sulphuric acid, using phenolphthalein as an indicator. One hundred cubic centimeters of the calcium hydroxide solution are then pipetted into a 200 cubic centimeter volumetric flask. A few drops of phenolphthalein solution are added, followed by normal sulphuric acid to acid reaction. Alcoholic potash (0.2 *N*) is then added, drop by drop, until a faint pink is produced. Distilled water that has previously been boiled to expel carbon dioxide is added to the mark.

The calcium sulphate solution thus prepared is used to standardize the pellets. Five of these, crushed in a mortar with a little distilled water, and 5 drops of phenolphthalein are added. The standard calcium sulphate solution is then added from a burette, until the last trace of phenolphthalein pink disappears. From the number of cubic centimeters used, and the determined strength of the calcium hydroxide solution, the strength of the pellets, expressed in term of calcium carbonate, is calculated.

Since a saturated solution of calcium hydroxide is about 0.04

N, the standard calcium sulphate solution as prepared above will be about 0.02 *N*, that is, 1 cubic centimeter will be equivalent to about 1 milligram of calcium carbonate.

The potassium palmitate tablets, as prepared above, will each be found equivalent to 1.5 to 2.0 milligrams of calcium carbonate.

These pellets should be standardized every week, as they lose strength fairly rapidly. What this loss of strength is due to is not yet certain, but from the data at hand it seems at least possible that it may arise from an acid fermentation of the glucose, bringing about a decomposition of the potassium palmitate with the separation of palmitic acid.

For use in the determination of total hardness, 1 cubic centimeter graduation marks were etched on a 100 cubic centimeter cylinder, so that volumes up to 105 cubic centimeters could be read. For a determination, 100 cubic centimeters of the water, measured in this cylinder, are transferred to a dry 250 cubic centimeter bottle (the glass-stoppered variety is convenient). A very small piece of methyl orange paper is suspended in the liquid by means of a platinum wire, while normal sulphuric acid is added from a dropping bottle until the paper becomes red. The paper is then removed to avoid coloring the liquid.

The liquid is then aspirated for five minutes with a continuous pressure bulb operated by hand. After aspiration, 1 cubic centimeter of phenolphthalein is added, followed by 0.2 *N* alcoholic caustic potash from a pipette, till a faint pink coloration develops. The liquid is now returned to the cylinder, the bottle being drained as completely as possible. The volume of the liquid is noted within 0.5 cubic centimeter. This will usually be between 102 and 105 cubic centimeters.

About 10 cubic centimeters of the liquid are then introduced into the mortar. One or more potassium palmitate pellets are then added, until an excess is present, that is, when a pronounced phenolphthalein coloration is produced. More water is then added from the cylinder, until the phenolphthalein coloration completely disappears. The volume of water used is noted. Several more pellets are then added, followed by water, till a second end point is reached. The two determinations should check each other within 0.5 to 1 cubic centimeter.

It is well to use four or five pellets in the two titrations to avoid any considerable error due to the lack of uniformity in the pellets.

To calculate the total hardness, it is first necessary to reduce the number of cubic centimeters of the water as used in the determination to the equivalent number of cubic centimeters of the original water, that is, before it was diluted with sulphuric acid, phenolphthalein, and alcoholic potash. Then the total hardness is computed from the value and number of the pellets used.

For example, let us suppose that the original volume of 100 cubic centimeters had been diluted to 104.5 cubic centimeters before titration with the palmitate pellets, each equivalent to 1.80 milligrams of calcium carbonate. Obviously the 48.5 cubic centimeters used for the determination are equal to

$$\frac{48.5 \times 100}{104.5} = 46.4$$

cubic centimeters of the original water.

Therefore the total hardness would be derived from the expression

$$\frac{1{,}000 \times 4 \times 1.80}{46.4}.$$

Or, using the data above, we may represent the entire calculation in one line as follows: Total hardness (as parts per million calcium carbonate) is equal to

$$\frac{10 \times 104.5 \times 4 \times 1.80}{48.5} = 155.$$

Total solids may be also estimated with the aid of Dole's formula,[5] slightly modified. For Philippine ground waters the following will be found satisfactory:

100 + normal carbonates (as Na_2CO_3) + bicarbonates (as $CaCO_3$) + 1.7 SO_3 + 1.6 Cl.

Estimated encrustants are calculated (for clear water) from Dole's formula:[6]

$$\text{Estimated encrustants} = \frac{\text{Bicarbonate alkalinity (as } CaCO_3) + CaSO_4 + \text{total hardness (as } CaCO_3)}{2}.$$

Assuming the sulphates to be present as calcium sulphate, the $CaSO_4$ in the above formula may be calculated as 1.7 SO_3. In this form the formula is available for field work.

Classification for boiler use is based upon the amount of estimated encrustants, as given by the American Railway Engineers' Maintenance of Way Association:[7]

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[5] Dole, R. B., *U. S. Geol. Surv., Water Supply Paper* (1916), No. 399, 304.

[6] *U. S. Geol. Surv., Water Supply Paper* (1910), No. 254, 232.

[7] *Proc. Am. Ry. Eng. & Maint. Way Assoc.* (1904), 5, 595.

TABLE V.—*Classification for boiler use.*

Parts per million.	
Less than 90	Good.
90 to 200	Fair.
200 to 430	Poor.
430 to 680	Bad.
Over 680	Very bad.

The use of the Berkefeld army filter to clarify turbid waters, as suggested by Leighton, has been discontinued in our field work for several reasons. Comparatively few of the waters examined on the average field trip are turbid. An analysis of only the clear portion of a turbid water is ordinarily not of great value, and when it is desired, a clear sample is readily obtained by sedimentation or by filtration through cotton or paper. Turbidity interferes appreciably only with the determination of sulphates. Its effect can be readily overcome by determining the turbidity of the liquid after adding hydrochloric acid and before adding barium chloride and subtracting this from the reading obtained after the sulphates have been precipitated. The difference represents the sulphate turbidity, and the amount of sulphates can be determined from the table without appreciable error. In short, the Berkefeld filter has found such limited application in our work that the minor benefits derived from its use have not been commensurate with the trouble and inconvenience of carrying it.

Accuracy of field determinations.—While field methods do not claim the exactness and accuracy possible in the laboratory, it is interesting to note that in several cases the values obtained by the two procedures do not differ very widely. As has been previously stated, results obtained in laboratory determinations are expressed in terms of two significant figures only. This mode of expression itself involves limits of accuracy that permit a maximum error of about 4 per cent. The average accuracy of field determinations, as stated by Leighton and confirmed in our own work, is roughly about 5 per cent. Turbidity shows the widest variation, ranging from about 3 per cent with turbidities of 500 to 1,000 parts per million to about 16 per cent with a turbidity of 30 parts per million, the deviation increasing fairly regularly with decreasing turbidities.

There are several sources of probable error of which the following are the most important:

When using a 100 cubic centimeter graduated cylinder, volumes cannot be read more accurately than to the nearest tenth of a cubic centimeter and often not that accurately. Further, when the mortar is washed with the water under examination, a certain amount remains in the mortar, which affects the volume subsequently employed for the next titration. Also the lack of uniformity in the pellets may introduce a very appreciable error.

In our own work additional sources of probable error have been encountered with "tabloid" methods. Our pellets are molded by hand and are, consequently, not as uniform as machine-made pellets. This is especially true of the potassium palmitate pellets, which form a sticky pill mass that dries very quickly and that is very difficult to mold uniformly. Again kaolin is used in the sodium carbonate and silver nitrate pellets and obscures the end points, thus decreasing the accuracy of the determinations.

In the "tabloid" determinations outlined above our methods differ from Leighton's in that, in the determination of chlorides and of total alkalinity, Leighton treated a known quantity of water with an excess of reagent to obtain an end point, while in all cases we titrate a known amount of reagent with the water to secure an end point. The former method gives values that lie between certain limits, as the excess of reagent is added in the form of parts of a pellet, and consequently the exact amount of reagent required for the titration is not determined. By making the excess small, the deviation from the true value is correspondingly decreased.

By our method, however, the exact titrating volume required is determined quickly and fairly accurately. The approach to the end point is thus reversed. This probably introduces an error in the determination of chlorides, which, however, is certainly much less than that involved in Leighton's method. It should be also remembered that the standardization of the pellets is made in the same manner as the field determination, thus decreasing the probable error. In the case of the determination of alkalinity, however, where methyl orange or butter yellow is employed as indicator, the reversed approach to the end point (that is, from acid to alkali) is theoretically the more correct of the two procedures and should, therefore, further increase the accuracy of the method as outlined above.

BACTERIOLOGICAL EXAMINATION

The bacteriological examination consists of two parts. One of these is a colony count made from two plate cultures. The other is a presumptive test for the presence of organisms of the *B. coli* group, which is made with one or more culture tubes.

The culture medium used in both cases is litmus lactose agar

(1.5 to 2.0 per cent agar, 1 per cent lactose). The reaction of this medium is almost neutral, there being present barely enough alkalinity to give a slight blue. It is put up in test tubes, in 10 cubic centimeter portions, and is thoroughly sterilized.

The Petri dishes used for the plate cultures are packed in individual envelopes and then sterilized. The envelopes, made of heavy Manila paper, are about the same width as the dishes and about twice as long as they are wide. Packages of six plates, well wrapped with paper, may be transported with little danger of breakage and will remain sterile indefinitely.

The pipettes used hold 1 cubic centimeter and are about 20 centimeters long. If these are not available, they may be readily made from glass tubing. The pipettes in lots of six are well wrapped in cheesecloth, having several folds of cloth between one pipette and the next. The ends of the package are tied together, and the package is inserted in a tin can just large enough for the purpose. The closed tin can containing the pipettes is then sterilized. While warm, the can is sealed with adhesive tape. When cool, the tape is well covered with paraffin. Pipettes so packed will remain sterile almost indefinitely.

For several kinds of work sterile bottles may be employed. Instead of the ordinary cotton plugs, which are often either pushed in or which come out during transportation, we use a cotton-covered cork. This arrangement has been found very satisfactory.

Ordinarily two plate cultures and one tube culture are made of each sample. Three tubes of media are thus required. The tubes are melted by heating in water over an alcohol lamp and are then cooled to 45°.

Plating is done at a temperature of from 40° to 43° C. For a water such as that from a spring or artesian well, believed to be comparatively pure, 0.5 and 1.0 cubic centimeter cultures are made. For a water suspected of contamination, plates may be made of 0.2, 0.1, or 0.05 cubic centimeter, depending on the apparent degree of contamination. The water is introduced into the Petri dish, the liquified agar is added, and the plate is manipulated to insure thorough mixing. After complete cooling, the plates are returned to their envelopes and carried in an inverted position to prevent spreading of the colonies by water of condensation.

The tube culture for the presumptive test is made by introducing the desired amount of water into the tube of liquified agar and mixing thoroughly by agitation. Usually 1 cubic centimeter is taken for this test, though more or less may be employed. The upper limit will be determined by the fact that 1 per cent agar is the weakest that solidifies on cooling to the temperatures ordinarily encountered (25° to 30° C.).

Incubation is at the ordinary temperature. No special apparatus is, therefore, required.

Colony counts are made both at the end of twenty-four and forty-eight hours, using a lens magnifying at least 5 diameters. The average of the two counts is the recorded value.

When the number of colonies is high, the plate is marked into sectors of convenient size, and the total number of colonies is estimated; or else the number on representative areas of 1 square centimeter is determined (a small card with openings of appropriate size and shape has been found very convenient for field work), and the necessary calculation for the total area is made. The presence of red colonies is noted.

The presence of the organisms of the colon group is indicated by the formation of gas in the tube cultures and by the formation of acid, as shown by the change of litmus from blue to red.

Summing up the whole question of the value of field methods, it might not be out of place to quote from the introduction of Leighton's paper:

> To the methods hereinafter proposed the term "assay" readily lends itself. There is no attempt at water analysis. The plan contemplates the determination of ingredients which give to water certain well-known characteristics. The methods have been found to be more nearly accurate than was at first anticipated, though this fact, it is believed, has not greatly increased their usefulness for the purposes in view. By their use, combined with a fair amount of common sense, the essential characteristics of waters can be ascertained at small expense. In almost every situation in which such determinations are significant they will afford sufficiently satisfactory data. In the case of finely balanced considerations of a purely physical, chemical, or geologic nature, however, they are practically useless. They are intended for practical purposes and have no place in pure science.

In the Philippines field methods have shown themselves to be both accurate and efficient. They have enabled the differentiation between good and bad waters used for domestic purposes, the selection of proper water for municipal supplies, the condemnation of dangerous sources of infection in cholera-infested districts, and the rapid evaluation of waters desired for industrial purposes.

ILLUSTRATION

PLATE I

FIG. 1. Apparatus used in a field assay of water.
2. The same, packed for transportation.

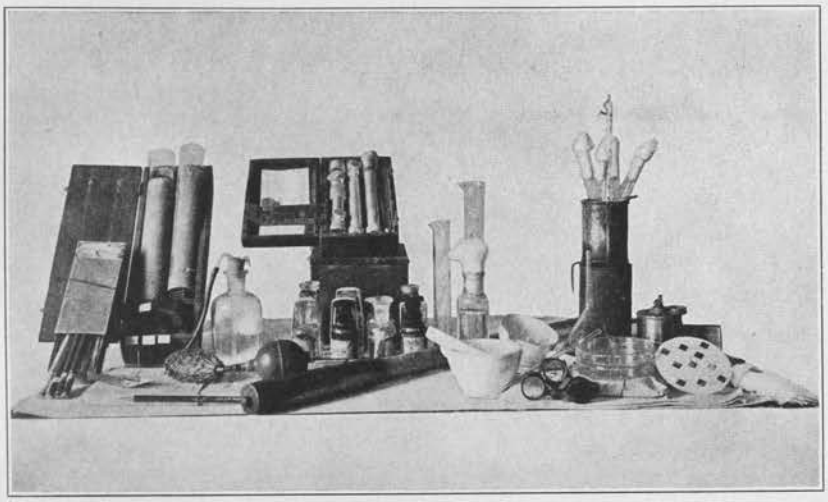

Fig. 1. Apparatus used in a field assay of water.

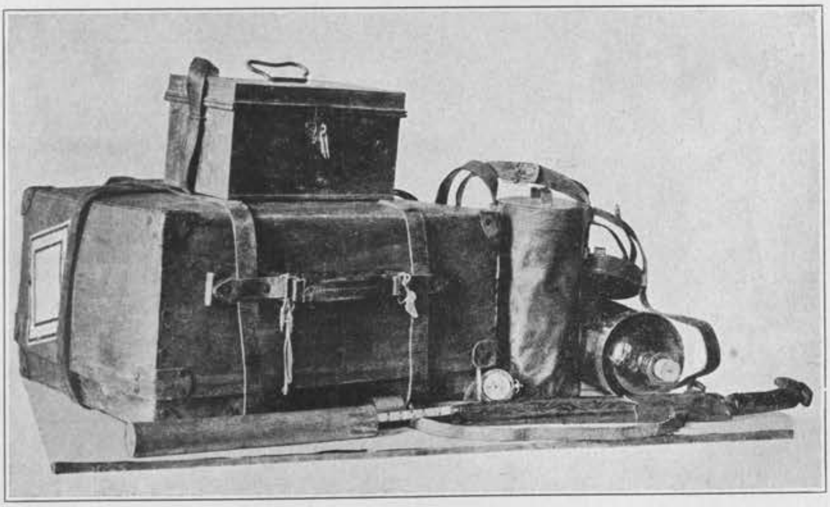

Fig. 2. The same, packed for transportation.

PLATE I.

TWO FIELD METHODS FOR THE DETERMINATION OF THE TOTAL HARDNESS OF WATER[1]

By A. S. BEHRMAN

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila)

In a field examination of the chemical quality of water the determination of total hardness is one of the most important analytical procedures. The data thus obtained, when used in conjunction with the results of the other commonly made determinations, give definite and quantitative information as to the nature of the most important of the dissolved constituents. This knowledge may be employed to advantage in connection with various problems related to water supplies, such as potability, purification, and industrial applications.

The Blacher method[2] for the determination of the total hardness of water by titration with potassium palmitate has been found to possess several marked advantages over the standard soap solution and similar procedures. It is clear-cut, accurate, and rapid.

Based on a study[3] of this method as applied to the analysis of typical Philippine waters, two field methods for the determination of hardness have been devised. Both are "tabloid" in nature, employing pellets of potassium palmitate instead of a solution of the reagent.

METHOD I

The first of these procedures is similar to Leighton's field modification[4] of the soap-solution method, in that the reagent is added in tablets of three strengths, until a sufficient excess is present to give a characteristic end reaction. Pellets of the same reacting values as those suggested by Leighton for sodium oleate are used, namely, 2.0, 1.0, and 0.5 milligrams of calcium carbonate, respectively.

One hundred cubic centimeters of the sample are measured into a 250 cubic centimeter bottle. A small piece of methyl

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[1] Received for publication September 11, 1917.

[2] Blacher, C., Grünberg, P., and Kissa, M., *Chem. Zeitg.* (1913), **37**, 56–8.

[3] Behrman, A. S., *This Journal, Sec. A* (1916), **11**, 291.

[4] Leighton, M. O., *U. S. Geol. Surv., Water Supply Paper* (1905), **No. 151**.

orange (or butter yellow) paper is suspended in the liquid by a hooked platinum wire, and normal sulphuric acid is added from a dropping bottle, until the indicator gives a decided acid reaction.[5] The paper is then removed from the bottle, to avoid absorption of the indicator. The solution is next strongly aspirated for five minutes, to remove carbon dioxide, using a continuous pressure atomizer bulb. When the aspiration has been effected, 1 cubic centimeter of phenolphthalein indicator solution (1 per cent) is added to the liquid by means of a 1 cubic centimeter bulb pipette. The acidity of the solution is neutralized with 0.2 *N* alcoholic potash, which is added drop by drop until a barely perceptible pink is observed.

The solution is now ready for treatment with the pellets of potassium palmitate. These are added in the same manner as in Leighton's method, using first the strong tablets and later the weaker ones, until an excess is present. The end point in this case is a deep phenolphthalein coloration.

A short cut that may be used advantageously in this method is to pour half of the solution to be treated with the pellets into another receptacle. Strong pellets are added rapidly to the portion in the bottle, until an excess has been provided. The remainder of the liquid is then returned to the bottle, after which the end point may be approached quickly, using the information gained in the treatment of the first portion.[6]

METHOD II

The second procedure differs from the first in that the end point is reached when an excess of the water, instead of potassium palmitate, is present. In addition, pellets of only one strength are employed, "whole" tablets being advantageously used.

A 100 cubic centimeter portion of the sample is acidified,

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[5] The addition of acid would, of course, be unnecessary in the case of a water with an acidity due to mineral acids. Such waters are extremely rare in the Philippines.

[6] From the number and strength of pellets used, the hardness of the water is readily calculated. Thus, if there were required 7 "whole," 3 "half," and 2 "quarter" tablets, having reacting values of 2.0, 1.0, and 0.5 milligrams of calcium carbonate, respectively, the total hardness, expressed in terms of parts per million of calcium carbonate, would be derived from the following expression:

$$\text{Total hardness} = \frac{1{,}000 \times [(7 \times 2.0) + (3 \times 1.0) + (2 \times 0.5)]}{100} = 180.$$

aspirated, and neutralized, exactly as in the first method. The liquid, thus prepared, is returned to the 100 cubic centimeter cylinder, and the volume is noted with the aid of graduation marks, etched on the cylinder at 1 cubic centimeter intervals to 105 cubic centimeters. The volume of the liquid should be read to the nearest 0.5 cubic centimeter. This will be usually found to be between 102 and 105 cubic centimeters.

In a small (100 cubic centimeter), heavily glazed porcelain mortar two or three pellets of potassium palmitate are crushed with 10 or 15 cubic centimeters of water from the cylinder. If an excess of the reagent is not indicated by the characteristic phenolphthalein coloration, more pellets are added until this condition is reached. More water is then added from the cylinder, slowly and with constant stirring, until the phenolphthalein coloration completely disappears, giving place to a creamy or yellowish white (depending on the amount of methyl orange absorbed during acidification). The end point is sharp and is easily determined. The volume required for the first end point is noted, reading to the nearest 0.5 cubic centimeter. Several more pellets are then added, preferably using the same number as before. Water is again supplied from the cylinder, until a second end point is obtained, and the amount used is noted. The two volumes should check within 0.5 cubic centimeter in fairly hard waters. Where a slightly larger difference is found, the mean of the two determinations may be employed in calculating the total hardness.[7]

PREPARATION AND STANDARDIZATION OF POTASSIUM PALMITATE TABLETS

Potassium palmitate being unavailable, it was prepared by the neutralization of an alcoholic solution of purified palmitic

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[7] The volume used in the determination is reduced to the volume of the original water, that is, before being diluted with acid, indicator, and alkali. The total hardness is then calculated from this corrected volume of water and from the number and strength of potassium palmitate tablets employed in the determination. Thus, if a 100 cubic centimeter portion of a given water was diluted to 103.5 cubic centimeters before treatment with potassium palmitate, and if, of this diluted volume, 42.5 cubic centimeters were required to react with 4 pellets of potassium palmitate, each equivalent to 2.0 milligrams of calcium carbonate, the total hardness, expressed as parts per million of calcium carbonate, would be found from the following expression:

$$\text{Total hardness} = \frac{10 \times 103.5 \times 4 \times 2.0}{42.5} = 195.$$

acid with a normal solution of alcohol potash. The resulting liquid was evaporated to dryness.

For the "whole" tablets 100 grams of finely powdered glucose are used with the potassium palmitate from 15 grams of palmitic acid. Corresponding amounts are employed for the weaker pellets. With the aid of a little distilled water, a homogeneous pill mass is made and is promptly molded to avoid changes in consistency. Where molding must be done by hand, a Whithall Tatum Company No. 2 tablet mold, which makes fifty pellets at one time, has been found satisfactory.

After being molded, the pellets are dusted with powdered talc; they are then dried, first in the air and then in a desiccator. They are subsequently packed in glass tubes, which hold about forty pellets and which are sealed with paraffin until desired for use.

The potassium palmitate pellets are standardized with a solution of calcium sulphate, prepared as follows from a saturated solution of calcium hydroxide: The normality of the calcium hydroxide is determined by titration with standard 0.1 *N* sulphuric acid. Into a 200 cubic centimeter volumetric flask are pipetted 100 cubic centimeters of the calcium hydroxide solution, and 1 cubic centimeter of phenolphthalein indicator solution is added. The solution is acidified with normal sulphuric acid and is then neutralized with 0.2 *N* alcoholic potash. Only a very faint phenolphthalein coloration should be present. Recently boiled, distilled water is now added to the mark.

Five of the pellets to be standardized are crushed in a mortar with a little distilled water, and phenolphthalein is added. This solution is titrated with the calcium sulphate, prepared as above, which is added drop by drop from a burette, with constant stirring. The end point is the disappearance of the phenolphthalein coloration,[8] just as in the field determination. From the mean of several such standardizations is calculated the reacting value of the pellets.

Unfortunately pellets of potassium palmitate lose their strength rather rapidly and must, therefore, be restandardized at frequent intervals. The exact cause of this deterioration is not as yet definitely known, but from the data at hand, it appears at least possible that the reason may be found in an acid fermentation of the glucose, in which a portion of the potassium palmitate is decomposed, with the separation of free palmitic acid.

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[8] It is essential, in preparing from palmitic acid the potassium palmitate to be used for pellets, that neutralization be effected with the slightest possible excess of alkali. If any appreciable amount of free alkali is present, the alkaline reaction to phenolphthalein will be due to this cause as well as to hydrolysis of the potassium palmitate and will not, therefore, disappear when an excess of calcium or magnesium salts is present.

It is possible that this objection may be overcome by the choice of a material more suitable than glucose. However, using the pellets made with glucose, it has been found very satisfactory to standardize the tablets weekly in the central laboratory in Manila and to supply the worker in the field with these data. A typical series of such standardizations is given in Table I.

TABLE I.—*Reacting values of "whole" potassium palmitate pellets. (Milligrams of calcium carbonate per pellet.)*

Date.	Reacting value.
April 4	1.68
April 12	1.59
April 27	1.52
April 30	1.49
May 7	1.43
May 14	1.33
May 21	1.22
May 28	1.06
June 5	0.89

The figures in Table I indicate a gradual and fairly uniform loss of strength in the pellets. In field investigations extending over comparatively short periods of time, reacting values may be obtained without serious error by interpolation. Where an extensive field study is planned, however, the method of periodic standardization in a central laboratory is preferable.

ACCURACY OF RESULTS AND COMPARISON OF METHODS

The first method described is essentially a field modification of Blacher's laboratory procedure and, therefore, has as its maximum accuracy that of the latter manipulation. From this must be subtracted the errors accruing from the field technic. Here the possible sources of error are the presence of a relatively large amount of glucose, the lack of uniformity of the pellets, the inaccuracy in reading volumes, and the fact that an excess of reagent is employed to obtain the end point.

The accuracy of the Blacher laboratory method has been found by a number of workers[9] to be about 2 to 3 per cent. That glucose does not introduce an error, in the quantities used, was shown in a series of experiments in which concentrations as high as 2 per cent of glucose—a condition not met with in practice—were employed without appreciably affecting the end point. Since volumes may be read to 0.1 cubic centimeter with a tall 100 cubic centimeter cylinder, the error involved here is also negligible. The error due to the excess of reagent present when an end point is obtained may be reduced to 1 or 2 per cent by making the excess small. The error due to lack of uniformity in the pellets may be placed at a like figure.

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[9] Zink, J., and Hollandt, F., *Zeitschr. f. angew. Chem.* (1914), 27, 439. Nochmann, E., *Pharm. Zentralh.* (1914), 55, 436–7. Behrman, A. S., loc. cit.

It is, therefore, reasonable to assume an error of about 5 per cent in using this method, an estimate that was verified in the case of several natural and artificially prepared waters. This degree of accuracy is ordinarily sufficient in questions of potability or of the suitability of a water for technical purposes.

No extensive comparison was made of results obtained from this method and those from gravimetric determinations. This was due to the fact that the first method was discontinued in favor of the second, as soon as the latter had been shown to be sufficiently accurate for field work.

The second procedure possesses three important advantages over the first:

(1) It is more rapid. The solution of the pellets in the first method requires considerable time. It was found that from fifteen to twenty minutes were required for a determination by the first method, while ten to twelve minutes sufficed for the second. (The five minutes employed in aspiration in both methods may be usually subtracted from the time of the analyst required, as this may be performed by an unskilled attendant.)

(2) Less reagent is needed. As only a part of the sample taken is treated with potassium palmitate, the second method will ordinarily require only a third or a fourth of the number of pellets required in the first.

(3) Several determinations may be rapidly made from the same sample, thus avoiding any gross error that may occur in a single determination.

The error of the second method is, like that of the first, about 5 per cent. It is believed that the accuracy of the method could be increased by machine-molding the pellets, thus securing greater uniformity, and by the selection of a material more suitable for binding and filling than glucose.

In Table II are shown the results of a number of field determinations of total hardness by the second method, compared with the calculated values of the same from gravimetric analyses of the calcium and magnesium contents.

TABLE II.—*Comparison of field and gravimetric determinations of total hardness.*[a]

No.	Calcium.	Magnesium.	Total hardness (calculated).	Total hardness (field method).	Error (per cent).
1	140	11	395	385	2.5
2	36	14	150	165	10.0
3	94	21	320	340	6.3
4	80	24	300	285	5.0
5	34	25	185	195	5.4
6	12	3.8	46	49	6.5
7	92	28	345	350	1.5
8	81	23	300	290	3.3
9	40	15	160	170	6.3
10	54	37	290	290	0.0
11	36	16	160	165	3.1
12	38	12	145	150	3.4
Average error					4.5

[a] The gravimetric determinations herein recorded were made by Mr. J. Gonzales y Nuñez, Inorganic chemist, Bureau of Science.

SUMMARY

Two methods have been described for the rapid determination in the field of the total hardness of water. Both methods have been shown to be applicable to field investigations, though preference has been given to the second procedure. The latter has been employed, with satisfactory results, for the past eight months in connection with the water survey made by the Bureau of Science.

SOME GENERALIZATIONS ON THE INFLUENCE OF SUBSTANCES ON CEMENT AND CONCRETE[1]

By J. C. WITT

(*From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila*)

The great variety of uses which modern industry is finding for concrete is continually presenting new problems for research and likewise increasing the importance of work that was completed at a time when the theoretical side was perhaps the only one under consideration. I refer especially to the sensitiveness of cement to many substances and to the destructive chemical action of some external agencies on concrete. The presence of any one of a number of organic or inorganic substances in the water or aggregates used in mixing concrete may seriously interfere with the work or later result in its failure. Even after concrete has been properly made and placed and the work has not failed in either quality or design, it sometimes happens that the construction is not permanent, because it comes into contact with some destructive substance.

This field of research is becoming more important year by year, because of the many new demands being made on the material. Sewer and drain pipe, storage tanks for various liquids, and even boats are now made of concrete. Therefore it is not surprising that the material should be called upon to resist conditions which were not known a few years ago. These agencies may be encountered in a number of ways. For instance, a sewer pipe may be capable of resisting the ordinary substances found in sewage, but may be injured by some industrial waste material which has found its way into the drainage system. Storage tanks may be constructed for a liquid in the belief that they will be satisfactory, but later it may be found that the liquid acts on the concrete, either injuring the tank or contaminating the liquid.[2]

It is highly desirable that as many substances as possible be investigated in relation to their effect on cement, so that the presence of harmful ones may be avoided in mixing concrete

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[1] Received for publication May 2, 1917.

[2] Cf. Rohland, P., *Beton u. Eisen* (1914), **13**, 341; Feuerungstechnic (1914), **2**, 360. Sartori, A., *Chem. Zeitg.* (1915), **39**, 957. Hinzlemann, R., *Journ. Soc. Chem. Ind.* (1904), **23**, 995.

and that the finished construction may be protected from them. Although it does not follow that the effect of a substance on cement as shown in the laboratory will necessarily be duplicated with concrete in practice, nevertheless such research is useful in indicating what substances are likely to cause trouble.

The literature since 1889, when Chandlot[3] made the important observation that certain substances affect the setting of cement, contains many papers on the subject. Some of these are simply reports of observed failures of concrete, while others are the result of much careful labor. At first it appears that the subject must be fairly well covered, but a study of the papers reveals that there is not much agreement among the various investigators. Table I shows an alphabetical list of electrolytes that have been studied relative to their effect on cement. When the same one is mentioned in more than one paper, the references have been arranged chronologically.

TABLE I.—*Effect of electrolytes on cement, as reported by a number of investigators.*

Aluminium chloride. Dobrzynski, Journ. Soc. Chem. Ind. (1892), **11**, 525.
A cement was gauged with water and with ammonium chloride solutions, ranging from 1 to 6 per cent. The lower concentration resulted in an increased tensile strength for 7-day briquettes, while the reverse was true with the higher concentrations. All the solutions lowered the strength of 28-day briquettes.

Aluminium chloride. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
The set was accelerated; no details are given.

Aluminium chloride. P. Rohland, Zeitschr. f. angew. Chem. (1903), **16**, 1049.
The original setting time of a cement was five hours and eight minutes. It was accelerated to one hour and eight minutes by using a 5.5 per cent aluminium chloride solution. With a 9 per cent solution the setting time was four hours and fifty-nine minutes.

Ammonium sulphate. L. Perin, Journ. Soc. Chem. Ind. (1906), **25**, 812.
Ammonium sulphate (0.86 per cent) has a greater influence on the set of cement than an equivalent amount of calcium sulphate (on the basis of the sulphuric anhydride content).

Barium chloride. Dobrzynski, Journ. Soc. Chem. Ind. (1892), **11**, 525.
A cement was gauged with a solution of barium chloride, ranging from 1 to 6 per cent. The tensile strength was considerably increased in every case.

Boric acid. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
The set was retarded; no details are given.

[3] Chandlot, *Journ. Soc. Chem. Ind.* (1889), **8**, 543.

Calcium chloride. Chandlot, Journ. Soc. Chem. Ind. (1889), **8**, 543.
The set was retarded.

Calcium chloride. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
The set was accelerated; no details are given.

Calcium chloride. N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.
Small amounts retard the set; large amounts accelerate it.

Calcium chloride. P. Rohland, Zeitschr. f. angew. Chem. (1903), **16**, 1049.
A cement gauged with calcium chloride solutions from 11.10 per cent to 25.90 per cent showed constantly decreasing setting time. The maximum change was from nine hours and thirty minutes to five hours.

Calcium chloride. R. C. Carpenter, Eng. Rec. (1904), **50**, 769.
An addition of 0.5 per cent produced the greatest retardation. This amount had no injurious effect on the ultimate strength.

Calcium chloride. O. von Blaese, Journ. Soc. Chem. Ind. (1907), **26**, 19.
The maximum retardation was produced with a 2 per cent solution.

Calcium chloride. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.
A small amount retards the set, but a large amount accelerates it.

Calcium chloride. Spielgeberg, Journ. Soc. Chem. Ind. (1909), **28**, 1131.
The effect varies with the composition and general properties of the cement.

Calcium chloride. H. Burchartz, Journ. Soc. Chem. Ind. (1910), **29**, 1108.
A small addition retards the set, while a larger one accelerates it. Four samples which were mixed with 20 per cent of the salt failed in soundness.

Calcium chloride. O. Kallauner, Z. Betonbau (1914), No. 2; Mitt. Cent. Förd. Deut. Port. Cement Ind., **3**, 213. [Chem. Abst. (1914), **8**, 2236.]
It decreases the strength. The author believes that all soluble calcium salts decompose cement.

Calcium chromate. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
It retards the set. No details are given.

Calcium hydroxide. R. C. Carpenter, Eng. Rec. (1904), **50**, 769.
Slaked lime (2 to 4 per cent), added to a cement which had become quick setting, restored it to normal.

Calcium nitrate. Chandlot, Journ. Soc. Chem. Ind. (1889), **8**, 543.
The set is retarded.

Calcium nitrate. O. Kallauner, Z. Betonbau (1914), No. 2; Mitt. Cent. Förd. Deut. Port. Cement Ind., **3**, 213. [Chem. Abst. (1914), **8**, 2236.]
There is a decrease in strength.

Calcium oxychloride. F. Hauenschild, Journ. Soc. Chem. Ind. (1902), **21**, 175.
The strength of specimens stored in air is increased, but the reverse is true of specimens stored in water.

Calcium sulphate. Chandlot, Journ. Soc. Chem. Ind. (1889), **8**, 543.
The set is retarded.

Calcium sulphate. L. Deval, Journ. Soc. Chem. Ind. (1902), **21**, 971.
It produces a change of form and an increase in volume with a tendency to diminish the tensile strength. It has no effect on nonaluminium cements nor on those low in calcium.

Calcium sulphate. R. C. Carpenter, Eng. Rec. (1904), **50**, 769.
The maximum setting time was obtained with an addition of 1.5 per cent.

Calcium sulphate. P. Rohland, Zeitschr. f. angew. Chem. (1905), **18**, 327.
The effect varies for nearly every cement, depending on the size of grain, the chemical composition, etc.

Calcium sulphate. L. Perin, Journ. Soc. Chem. Ind. (1906), **25**, 812.
Plaster of paris and raw gypsum (containing equivalent amounts of sulphuric anhydride) have the same effect.

Calcium sulphate. Spiegelberg, Journ. Soc. Chem. Ind. (1909), **28**, 1131.
The effect varies from the composition of the cement.

Calcium sulphate. W. C. Reibling and F. D. Reyes, Phil. Journ. Sci., Sec. A (1911), **6**, 225.
The maximum retardation is produced with 2 to 3 per cent of calcium sulphate.

Calcium sulphate. O. Kallauner, Z. Betonbau (1914), No. 2; Mitt. Cent. Förd. Deut. Port. Cement Ind., **3**, 213. [Chem. Abst. (1914), **8**, 2236.]
Temporarily the strength is increased.

Calcium sulphate. J. C. Witt, and F. D. Reyes, Phil. Journ. Sci., Sec. A (1917), **12**, 133.
Six brands of cement were tested with additions of calcium sulphate. In general, the maximum retardation of set was produced by 1.5 to 2 per cent sulphuric anhydride. Lower tensile strength and high expansion in sea water resulted when more than 3 per cent was present.

Calcium sulphide. N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.
Calcium sulphide forms an insoluble compound with calcium hydroxide, but the effect is relatively low, because about 3 parts of the sulphide are required to combine with 1 part of the hydroxide.

Calcium sulphate. O. Kallauner, Z. Betonbau (1914), No. 2; Mitt. Cent. Förd. Deut. Port. Cement Ind., **3**, 213. [Chem. Abst. (1914), **8**, 2236.]
Temporarily the strength is increased.

Calcium thiosulphate. O. Kallauner, Z. Betonbau (1914), No. 2; Mitt. Cent. Förd. Deut. Port. Cement Ind., **3**, 213. [Chem. Abst. (1914), **8**, 2236.]
Temporarily the strength is increased.

Carbon dioxide (aqueous solution). N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.

A pronounced accelerating effect is noted, though the solubility of the gas in water is low.

Carbon dioxide. C. Montemartini, Journ. Soc. Chem. Ind. (1908), **27**, 228.

When dry, cement is treated with a current of dry carbon dioxide; no change is apparent.

Ferrous sulphate. French patent 408,060, Journ. Soc. Chem. Ind. (1910), **29**, 631.

The addition of 1 to 3 per cent ferrous sulphate is said to quicken the set and increase the strength.

Lithium chloride. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.

There is no effect.

Magnesium chloride. Dobrzynski, Journ. Soc. Chem. Ind. (1892), **11**, 525.

The concentration of the solutions was from 1 to 6 per cent. The lower percentages causes a slight increase in tensile strength, while the higher ones causes a slight decrease.

Magnesium chloride. O. von Blaese, Journ. Soc. Chem. Ind. (1907), **26**, 19.

The maximum setting time is obtained with 6 per cent of the salt.

Potassium aluminium sulphate. L. Perrin, Journ. Soc. Chem. Ind. (1906), **25**, 812.

When cement is mixed with 1.54 per cent of the salt, the setting time is unchanged. The author believes that the presence of aluminium is responsible for the negative effect.

Potassium carbonate. N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.

No comments are made.

Potassium dichromate. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.

The set is retarded. No details are given.

Potassium dichromate. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.

The set is retarded.

Potassium sulphate. P. Rohland, Zeitschr, f. angew. Chem. (1903), **16**, 1049.

The set is retarded or accelerated, depending on conditions.

Sodium bisulphite. H. Luftschitz, Tonind-Zeitg. (1913), **37**, 1986.

The salts were mixed with cement in various proportions from 0.5 to 4 per cent, and tests were made for tensile and compressive strength. The strength of the specimens decreases with increased amount of salts.

Sodium borate. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.

The set is retarded. No details are given.

Sodium borate. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.

The set is retarded.

Sodium carbonate. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
The set is accelerated. No details are given.

Sodium carbonate. N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.
No comments are made.

Sodium carbonate. P. Rohland, Zeitschr. f. angew. Chem. (1903), **16**, 1049.
The set is first retarded and then accelerated. The results were similar but different in degree for the several cements investigated.

Sodium carbonate. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.
The set is accelerated.

Sodium chloride. Chandlot, Journ. Soc. Chem. Ind. (1889), **8**, 543.
It has no influence on either set or tensile strength.

Sodium chloride. Dobrzynski, Journ. Soc. Chem. Ind. (1892), **11**, 525.
Sodium chloride solutions from 1 to 6 per cent were employed; most of them caused a slight increase in the 7-day strength and a slight decrease in the 28-day strength.

Sodium chloride. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
It has no effect. No details are given.

Sodium chloride. N. Ljamin, Journ. Soc. Chem. Ind. (1902), **21**, 972.
No comments are made.

Sodium chloride. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.
Small quantities have no effect.

Sodium chloride. A. Passow, Tonind. Zeitg. (1914), **38**, 995.
Strength is increased by adding 0.5 to 1 per cent sodium chloride by immersing the specimens in a salt solution. The effect is attributed to the increased solubility of calcium hydroxide in sodium chloride solution.

Sodium sulphate. P. Rohland, Ber. d. deutsch. chem. Ges. (1901), **33**, 2831.
The set is retarded. No details are given.

Sodium sulphate. P. Rohland, Journ. Soc. Chem. Ind. (1909), **28**, 23.
The set is retarded.

Sodium sulphide. J. C. Witt, Phil. Journ. Sci., Sec. A (1916), **11**, 273.
Small amounts retard the set, but larger amounts accelerate it.
The tensile strength is decreased. In general, the cements highest in iron are most affected.

Table I reveals that, regardless of the value of each paper when considered alone, the general subject shows little progress.[4] Aside from certain substances which have been investigated in great detail by a number of workers—such as calcium sulphate—it is impossible to find much definite information in the literature. In some cases an electrolyte has been investigated by only one worker. As a rule, one paper does not cover sufficient ground to make the work of general value. This is true of boric acid, barium chloride, calcium oxychloride, calcium thiosulphate, and lithium chloride. When a substance has been investigated by a number of persons, it often happens that conflicting statements are published. According to Chandlot and Rohland,[5] sodium chloride has no effect on cement, but Dobrzynski and Passow say that it increases the tensile strength. Rohland classes sodium carbonate as an accelerator of the set of cement, while in a previous paper he stated that it might either retard or accelerate it. Similar disagreements on the effect of calcium chloride mav be found, though its general effect on the set has been established. One interesting example of disagreement is that of ferrous compounds. Desch[6] is of the opinion that if any ferrous iron is present in cement it may be converted into ferrous sulphide by calcium sulphide, which is produced by the reducing action of the fuel. Ferrous sulphide is considered objectionable because of its ability to become oxidized, which would result in a change in volume. However, there is a French patent for the right to add from 1 to 3 per cent dry ferrous sulphate to cement. It is claimed that this will accelerate the set and increase the strength. The general effect of calcium sulphate is perhaps better known than that of any other substance, because so much research has resulted from its use in the manufacture of cement. However, there are still many conflicting views on the rôle of the substance in controlling the set and the amount that can be added without endangering the quality.[7]

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[4] Cf. Desch, C. H., The Chemistry and Testing of Cement. Edward Arnold, London (1911), 127.

The causes that have thus far prevented many of the investigations carried on by various workers from being comparable may be divided into two classes:

1. Details that either cannot be controlled by the investigator or which can be controlled only with considerable difficulty. These include the individual characteristics of cements, resulting from the composition of the raw materials and the methods of manufacture; the personal equation of the investigator; variations in temperature and humidity due to change of season and to location; and differences in apparatus and methods of procedure in various countries. Most of these points do not require explanation. It is well known that cements of the same chemical analysis may be entirely different in their physical properties. While it would be possible to control the temperature and humidity of laboratories so that cement could always be tested

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[5] See Table I.

[6] Desch, C. H., op. cit., 75.

[7] Cf. Witt, J. C., and Reyes, F. D., *This Journal, Sec. A* (1917), 12, 133.

under the same conditions, the time and expense would be hardly justified.

2. Details which can be easily controlled by the investigator. These include the adoption of some definite plan for the work, so that results obtained with different substances may be directly comparable in so far as the concentration and purity of the solutions employed are concerned; analysis and physical tests of all cements as received; the choice of a sufficient number of cements so that results may be considered as averages.

Chemical and physical tests of all cements investigated should be made because the results may point out the constituent of the cement that is most concerned in the observed results. The conditions under which work is carried on, including the average temperature, humidity, and laboratory methods, should be given because they are of recognized importance. As a rule, solutions are made on the percentage basis and are not afterward analyzed. The results obtained are not directly comparable in some respects. For instance, it usually happens that no account is taken of atomic weights and valencies. An investigator may make solutions of aluminium chloride and sodium chloride and compare results obtained by the same percentage concentrations of each, and yet aluminium chloride contains a much higher percentage of chlorine than does sodium chloride. Likewise in comparing the relative effects of calcium chloride and calcium sulphate the percentage basis is not the proper one.

It is apparent that much progress cannot be made in this field of investigation until the results of various workers can be connected by certain generalizations. The points of basic importance are:

1. Does the effect of an electrolyte depend on the negative ion, the positive ion, or on both?
2. Is the degree of solubility of the corresponding calcium salt important?
3. Can the effect of an untried electrolyte be predicted from results obtained with others?
4. Can the observed effect be traced to any particular constituent of the cement?

When 1 and 2 have been determined for a large number of electrolytes, it should be possible to predict the effect of an untried electrolyte—at least qualitatively—on many cements. Number 4 is of great practical importance. Such data could be used as a factor in determining the cement best suited for construction that is to be exposed to certain conditions. This has been already taken advantage of in the study of the effect of sea water on cement. It has been shown for some cements that the iron content is one of the factors which determines the effect of sodium sulphide.[8]

This paper presents experiments that have been undertaken in an effort to correlate investigations in this field of research.

EXPERIMENTAL WORK

Two barrels each of four brands of cement were chosen. Each barrel was carefully sampled, and the cement was then preserved in suitable containers during the progress of the work. The results of the chemical analysis and the physical tests of the cements as received in the laboratory are given in Tables II and III.

TABLE II.—*Chemical analysis of cements.*

[Numbers give percentages.]

	I.	II.	III.	IV.
Loss on ignition	2.43	2.15	2.17	3.24
Silica (SiO_2)	22.60	21.40	21.26	20.62
Alumina (Al_2O_3)	7.72	7.58	8.54	6.62
Ferric oxide (Fe_2O_3)	1.76	1.70	2.08	2.56
Calcium oxide (CaO)	61.32	62.94	62.82	63.50
Magnesia (MgO)	1.08	1.37	1.13	1.43
Sulphuric anhydride (SO_3)	1.45	1.61	1.02	0.82
Sodium and potassium oxides (Na_2O, K_2O)	1.63	1.14	1.17	1.33

TABLE III.—*Physical tests of cements as received.*

Brand.	Fineness.		Specific gravity.	Initial set.	Final set.	Tensile strength in kilos per square centimeter.			Tensile strength in pounds per square inch.		
	200-mesh.	100-mesh.				7 days.	28 days.	180 days.	7 days.	28 days.	180 days.
				Hrs. min.	*Hrs. min.*						
I	81.1	97.0	3.12	4 5	6 48	18.7	25.3	25.6	267	359	365
II	83.7	97.0	3.10	3 56	5 44	19.7	24.6	26.2	280	351	373
III	85.7	98.2	3.12	3 36	6 12	22.5	27.4	29.0	321	389	413
IV	83.7	89.4	3.10	3 46	6 47	15.4	20.9	26.2	218	297	373

The following electrolytes were chosen:

Sodium chloride.
Zinc chloride.
Copper chloride.
Sodium nitrate.
Potassium nitrate.
Ammonium nitrate.
Sodium sulphate.
Zinc sulphate.
Copper sulphate.
Sodium bicarbonate.
Potassium bicarbonate.

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[8] Op. cit.

If a cement is gauged with solutions of several chlorides, containing the same amount of chlorine per liter, it should give the same results, aside from the experimental error, as far as the chlorine ion is concerned. In the same way, if we gauge a cement with solutions of several salts of sodium, for example, having the same amount of sodium per liter, we have a basis for comparing the effect of the negative ion. Further, by using a number of salts that form soluble calcium compounds and a number of others that produce difficultly soluble calcium compounds, we should be able to obtain data on the question of whether or not there is any relation between the effect of electrolytes and the solubility of the calcium compounds which they produce.

A stock solution of each electrolyte was first made and standardized. This was normal on the basis of the negative ion. Various dilutions were then made as needed. Care was taken to choose no electrolyte that contained the principal metallic elements found in cement, such as calcium and aluminium, or any that contained metals that might assume the same rôle, such as iron and magnesium. The data on all solutions employed are given in Table IV.

Mortar briquettes were made from each cement, using water and four concentrations of each of the eleven solutions mentioned; also setting time[9] and soundness tests were made on each cement with each solution. The approximate average temperature was 30° C., and the average relative humidity was about 80 per cent. All the tests were made in accordance with United States Government specifications for Portland cement.[10] The normal consistency of each cement was determined with the various solutions. The results are shown in Table V, VI, and VII.

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[9] Each cement used in this investigation contains calcium sulphate. Consequently when a cement is gauged with a solution of an electrolyte, the observed setting time may be included the resultant of the effect of the two substances.

[10] See Circular 33, United States Bureau of Standards, Washington, Government Printing Office (1912).

TABLE IV.—*Data on solutions employed.*

Salt.	Normality.	Grams of salt per cubic centimeter (by analysis).	Centimeters of solution required for normal consistency.[a]	Parts by weight per 100 grams of cement.		
				Of salt.	Of positive radical.	Of negative radical.
Sodium chloride	0.05	0.0029	22	0.0640	0.0252	0.0388
	0.10	0.0058	23	0.1339	0.0527	0.0812
	0.50	0.0291	23	0.6695	0.2634	0.4061
	1.00	0.0582	22	1.2810	0.5040	0.7770
Zinc chloride	0.05	0.0034	22	0.0753	0.0361	0.0392
	0.10	0.0068	23	0.1575	0.0756	0.0819
	0.50	0.0342	23	0.7874	0.3779	0.4095
	1.00	0.0685	22	1.5065	0.7226	0.7839
Copper chloride	0.05	0.0034	22	0.0741	0.0351	0.0390
	0.10	0.0067	23	0.1549	0.0732	0.0817
	0.50	0.0337	23	0.7745	0.3663	0.4082
	1.00	0.0674	22	1.4824	0.7011	0.7813
Sodium nitrate	0.05	0.0043	22	0.0937	0.0253	0.0684
	0.10	0.0085	23	0.1959	0.0530	0.1419
	0.50	0.0426	23	0.9795	0.2650	0.7145
	1.00	0.0852	22	1.8739	0.5069	1.3670
Potassium nitrate	0.05	0.0051	22	0.1116	0.0432	0.0684
	0.10	0.0102	23	0.2334	0.0904	0.1430
	0.50	0.0508	23	1.1670	0.4520	0.7150
	1.00	0.1015	22	2.2332	0.8646	1.3686
Ammonium nitrate	0.05	0.0040	22	0.0883	0.0199	0.0684
	0.10	0.0080	23	0.1846	0.0416	0.1430
	0.50	0.0401	23	0.9230	0.2079	0.7151
	1.00	0.0803	22	1.7659	0.3978	1.3681
Sodium sulphate	0.05	0.0036	22	0.0785	0.0254	0.0531
	0.10	0.0071	23	0.1643	0.0532	0.1111
	0.50	0.0357	23	0.8215	0.2661	0.5554
	1.00	0.0714	22	1.5719	0.5091	1.0628
Zinc sulphate	0.05	0.0040	22	0.0886	0.0359	0.0527
	0.10	0.0081	23	0.1852	0.0751	0.1101
	0.50	0.0403	23	0.9260	0.3753	0.5507
	1.00	0.0806	23	1.7721	0.7181	1.0540
Copper sulphate	0.05	0.0040	22	0.0881	0.0351	0.0530
	0.10	0.0080	23	0.1843	0.0734	0.1109
	0.50	0.0401	23	0.9215	0.3672	0.5543
	1.00	0.0801	22	1.7628	0.7025	1.0603
Sodium[b] bicarbonate	0.05	0.0020	22	0.0447	0.0125	0.0316
	0.10	0.0041	23	0.0935	0.0262	0.0661
	0.50	0.0208	22	0.4472	0.1259	0.3163
	1.00	0.0407	22	0.8947	0.2509	0.6327
Potassium[b] bicarbonate	0.05	0.0024	22	0.0538	0.0185	0.0318
	0.10	0.0049	23	0.1126	0.0449	0.0663
	0.50	0.0245	23	0.5629	0.2246	0.3319
	1.00	0.0489	22	1.0769	0.3706	0.6365

[a] The normal consistency values given in this column are averages for the four cements. In nearly every case the variation was only 1 or 2 per cent. In gauging cement IV with 0.50 *N* copper sulphate and with 0.50 *N* potassium bicarbonate, however, the normal consistency was unusually high, being 26 and 28 per cent, respectively. These two values were not counted in the averages given here.

[b] The concentrations of these solutions are based on the amount of CO_3 present. They are only half the indicated concentrations with respect to alkalinity.

TABLE V.—*Effect on tensile strength (1:3 mortar).*

KILOGRAMS PER SQUARE CENTIMETER.

Solution.	Normality.	Cement I.			Cement II.			Cement III.			Cement IV.		
		7 days.	28 days.	180 days.	7 days.	28 days.	180 days.	7 days.	28 days.	180 days.	7 days.	28 days.	180 days.
Water		18.8	25.2	25.6	19.7	25.0	26.2	22.6	27.3	29.0	15.3	20.9	26.2
Sodium chloride	0.05	15.0	18.5	17.2	14.1	16.7	19.0	18.8	23.2	24.1	12.7	18.5	22.7
	0.10	14.3	20.9	23.5	14.8	20.5	22.1	14.7	20.4	24.9	10.7	15.4	22.0
	0.50	17.1	23.2	28.1	19.3	21.5	26.7	16.4	21.7	24.6	10.4	20.4	22.8
	1.00	18.8	27.2	29.5	16.5	20.8	25.3	21.3	26.6	26.2	13.8	16.6	22.8
Zinc chloride	0.05	16.5	19.3	20.8	14.8	18.8	19.8	18.6	24.2	26.1	13.7	18.6	24.9
	0.10	14.9	16.2	23.2	17.7	22.9	24.2	19.2	22.6	29.5	10.9	17.5	22.1
	0.50	18.5	27.5	32.7	19.9	27.8	33.2	20.7	27.9	30.1	16.3	20.7	29.2
	1.00	17.1	24.1	33.3	17.6	23.4	30.2	20.5	25.9	25.6	13.8	21.6	30.5
Copper chloride	0.05	15.4	20.7	23.2	12.7	17.8	19.0	15.2	27.4	24.7	11.9	14.2	25.6
	0.10	15.6	22.9	21.7	14.2	18.4	26.1	16.2	22.4	28.8	9.9	16.2	22.5
	0.50	9.8	26.0	31.6	10.7	25.4	29.4	17.5	24.5	31.6	6.9	15.9	25.7
	1.00	12.2	22.4	33.3	17.1	23.4	28.5	17.4	28.2	31.8	12.9	19.9	27.7
Sodium nitrate	0.05	14.4	20.4	22.1	14.9	16.7	19.1	19.1	24.7	24.9	11.6	16.3	24.0
	0.10	13.6	21.0	21.8	16.3	21.2	23.5	15.0	23.8	26.4	9.1	12.3	21.5
	0.50	19.1	28.2	30.6	16.4	21.5	25.4	13.5	21.2	23.9	7.4	11.7	20.4
	1.00	13.0	22.0	27.0	13.7	20.4	23.9	12.5	21.0	26.3	9.2	16.3	23.5
Potassium nitrate	0.05	14.7	18.4	19.9	13.3	17.9	19.2	19.7	23.6	23.9	11.6	16.7	21.0
	0.10	15.1	19.7	25.6	15.9	22.9	24.3	16.5	23.6	25.5	9.5	12.7	20.4
	0.50	13.7	18.7	25.3	14.4	20.7	23.8	11.8	17.2	22.9	8.1	12.5	21.8
	1.00	15.2	21.1	23.6	14.3	20.3	22.1	17.5	21.8	22.1	9.7	14.2	22.5
Ammonium nitrate	0.05	15.6	20.2	20.4	17.0	18.9	20.1	18.8	23.1	22.8	11.8	17.4	24.2
	0.10	17.5	21.5	24.5	17.0	20.2	22.0	15.7	22.8	22.8	9.2	13.6	21.0
	0.50	16.4	22.3	31.6	21.0	25.6	29.4	14.7	23.9	26.2	8.9	13.9	23.5
	1.00	21.2	28.3	30.9	20.6	27.4	27.1	19.1	23.2	33.0	12.0	18.9	25.6

Sodium sulphate	0.05	14.8	19.4	20.3	15.7	20.1	22.9	21.2	28.8	34.1	12.5	16.0	22.5
	0.10	16.8	22.2	23.6	16.8	20.1	23.9	18.7	22.7	23.6	10.5	15.5	22.1
	0.50	14.0	21.6	26.0	17.3	24.9	25.6	12.8	19.8	26.0	9.8	14.3	24.2
	1.00	21.5	27.0	31.6	21.1	25.0	29.5	19.8	24.2	30.2	15.7	22.7	27.7
Zinc sulphate	0.05	13.0	18.7	20.3	18.1	22.7	22.0	18.5	27.0	27.5	14.1	18.4	23.9
	0.10	17.7	22.3	25.2	16.3	21.9	25.3	18.8	23.4	26.0	12.8	17.5	24.6
	0.50	21.6	30.2	33.0	19.9	25.7	33.3	17.6	25.6	31.0	15.9	23.8	29.2
	1.00	7.4	27.0	36.8	18.5	27.1	32.6	21.0	29.0	31.7	19.1	25.8	29.5
Copper sulphate	0.05	17.7	23.2	24.6	15.1	24.2	25.3	19.4	25.7	26.2	12.7	19.8	25.3
	0.10	14.3	23.1	25.2	5.4	20.8	21.7	17.7	24.7	24.6	11.5	16.5	22.5
	0.50	7.6	25.7	34.7	13.4	23.9	32.3	11.7	21.9	27.6	8.4	19.9	27.4
	1.00	3.9	19.7	30.2	10.9	25.4	27.7	18.0	29.7	36.8	9.4	22.2	28.1
Sodium bicarbonate	0.05	19.8	23.8	25.6	17.0	18.4	19.3	19.6	24.0	24.6	12.0	17.3	23.9
	0.10	13.4	20.1	24.1	19.0	20.1	21.8	15.6	21.7	22.9	10.3	16.0	24.2
	0.50	14.1	22.1	28.4	15.7	21.9	26.0	12.1	18.5	25.9	6.0	10.3	19.9
	1.00	17.8	23.5	31.6	17.7	22.7	22.7	15.9	21.6	25.6	12.9	16.4	17.3
Potassium bicarbonate	0.05	61.4	23.3	25.0	15.9	17.5	20.3	19.7	25.5	26.0	14.4	16.6	24.6
	0.10	13.7	19.0	23.2	17.1	22.6	24.8	17.7	23.3	25.6	11.5	15.2	23.9
	0.50	17.8	25.9	29.5	17.1	21.3	27.7	13.1	18.0	25.5	6.8	7.6	19.3
	1.00	19.1	24.1	27.0	16.4	21.7	24.2	17.3	21.7	25.3	10.6	17.4	19.4

TABLE V.—*Effect on tensile strength (1:3 mortar)*—Continued.

POUNDS PER SQUARE INCH.

Solution.	Normality.	Cement I.			Cement II.			Cement III.			Cement IV.		
		7 days.	28 days.	180 days.	7 days.	28 days.	180 days.	7 days.	28 days.	180 days.	7 days.	28 days.	180 days.
Water		267	359	365	280	351	373	321	389	413	218	297	373
Sodium chloride	0.05	214	264	246	202	238	269	268	330	343	182	264	323
	0.10	205	296	335	210	292	316	208	290	355	153	218	313
	0.50	243	330	401	275	307	379	233	308	349	149	290	324
	1.00	267	387	421	235	295	359	303	378	373	197	236	324
Zinc chloride	0.05	235	275	295	210	267	282	265	345	372	196	265	356
	0.10	212	230	329	252	327	344	273	321	420	156	249	315
	0.50	263	393	467	284	396	473	293	397	428	231	294	417
	1.00	244	344	476	250	333	430	391	368	365	197	307	436
Copper chloride	0.05	218	294	331	183	254	270	216	390	352	170	203	365
	0.10	221	326	308	203	262	372	230	319	409	141	230	321
	0.50	140	370	450	153	361	418	249	348	450	99	226	367
	1.00	176	319	474	244	333	407	247	403	453	185	284	395
Sodium nitrate	0.05	206	290	316	211	238	272	271	352	354	166	232	342
	0.10	195	298	310	231	301	336	213	339	377	130	176	307
	0.50	272	401	437	233	307	362	194	302	340	107	168	291
	1.00	187	313	386	196	290	339	179	299	374	132	232	336
Potassium nitrate	0.05	209	261	283	190	255	273	280	337	341	166	238	298
	0.10	215	280	364	227	326	347	235	336	363	136	182	291
	0.50	197	266	361	208	293	338	168	245	327	116	179	309
	1.00	217	300	337	207	289	315	249	310	316	139	203	319
Ammonium nitrate	0.05	221	288	290	241	268	287	267	329	326	169	247	345
	0.10	249	306	348	242	288	313	224	325	325	133	195	298
	0.50	233	318	415	299	365	418	208	340	373	127	199	334
	1.00	301	404	439	292	390	387	272	330	469	171	268	366

Sodium sulphate	0.05	210	277	288	223	286	327	302	410	487	179	228	321
	0.10	239	316	337	239	286	340	266	324	337	150	220	316
	0.50	200	308	370	246	355	364	184	231	370	140	205	345
	1.00	306	385	449	300	356	421	282	345	430	223	323	396
Zinc sulphate	0.05	186	266	288	258	323	313	263	385	392	201	262	341
	0.10	251	318	358	231	311	359	267	334	370	183	248	349
	0.50	309	430	469	283	366	475	250	365	442	226	338	417
	1.00	107	385	524	263	386	466	300	413	452	272	367	419
Copper sulphate	0.05	252	330	351	250	345	361	277	366	373	182	281	361
	0.10	205	329	353	219	295	308	252	352	351	165	235	321
	0.50	108	366	495	191	340	461	168	311	393	120	284	391
	1.00	56	280	413	156	362	394	258	423	526	135	316	400
Sodium bicarbonate	0.05	282	339	365	242	262	276	278	342	349	171	246	339
	0.10	191	287	343	270	287	310	221	308	327	147	227	345
	0.50	201	315	406	224	311	370	173	264	368	195	147	283
	1.00	254	335	415	251	323	323	226	307	365	185	234	247
Potassium bicarbonate	0.05	234	331	357	226	249	288	280	363	370	207	236	351
	0.10	197	270	330	243	321	353	251	332	365	165	216	339
	0.50	253	369	421	243	303	394	188	256	363	98	109	274
	1.00	272	343	384	234	308	346	246	309	360	152	247	277

TABLE VI.—*Effect on initial set.*[a]

Brand.	Gauged with water.	Normality of solution.	Sodium chloride.	Zinc chloride.	Copper chloride.	Sodium nitrate.	Potassium nitrate.	Ammonium nitrate.	Sodium sulphate.	Zinc sulphate.	Copper sulphate.	Sodium bicarbonate.	Potassium bicarbonate.
4 05-16.48	*Hrs. min.*		*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*
I 3.56 5.44	4 5	0.05	6 10	6 2	7 26	5 43	6 35	6 27	6 20	6 38	6 29	6 20	5 47
		0.10	4 24	4 59	11 37	4 17	4 17	4 17	4 15	4 48	12 39	4 41	4 45
		0.50	5 5	10 9	14 23	4 33	4 55	4 12	4 27	5 26	14 40	5 0	4 55
		1.00	5 54	26 9	19 50	4 31	5 30	5 52	4 30	6 25	19 45	4 25	3 30
II 3.36 6.12	3 36	0.05	7 13	7 9	6 52	5 49	6 20	5 41	5 37	7 37	7 24	5 58	6 13
		0.10	6 11	15 42	15 17	6 38	5 45	6 13	6 1	14 35	16 11	6 36	6 25
		0.50	5 8	10 7	10 41	5 14	5 23	4 1	5 0	14 58	15 0	5 22	5 20
		1.00	4 6	24 22	22 3	3 40	5 9	2 40	3 44	28 0	26 37	3 28	3 12
III 3.46 6.07	3 36	0.05	5 42	7 22	5 14	5 11	4 50	4 28	4 53	6 4	5 45	4 25	5 4
		0.10	4 20	8 27	8 24	4 0	4 3	4 24	5 33	6 40	9 4	4 35	4 29
		0.50	5 4	6 40	6 40	3 56	4 20	4 13	4 31	7 30	10 45	4 15	4 15
		1.00	4 26	25 3	6 47	4 15	3 52	4 10	3 44	25 49	14 48	2 22	4 11
IV	3 46	0.05	6 27	7 7	7 30	6 25	5 36	5 31	6 7	8 3	8 19	6 23	6 2
		0.10	6 16	9 52	12 14	6 15	6 3	5 45	5 55	8 58	9 45	5 41	6 14
		0.50	7 8	9 50	15 7	5 49	7 16	6 7	7 0	7 52	15 17	3 52	5 6
		1.00	5 32	25 53	33 47	4 1	5 35	5 1	4 46	24 42	46 37	2 14	3 3

[a] Gillmore needles were used. When less than eight hours, the setting-time results are accurate to probably ten or fifteen minutes. When the set is very slow, as in some of the cases here shown, the result depends largely on the judgment of the operator and may be considered only approximate.

TABLE VII.—*Effect on final set.*

Brand.	Gauged with water.	Normality of solutions.	Sodium chloride.	Zinc chloride.	Copper chloride.	Sodium nitrate.	Potassium nitrate.	Ammonium nitrate.	Sodium sulphate.	Zinc sulphate.	Copper sulphate.	Sodium bicarbonate.	Potassium bicarbonate.
	Hrs. min.		*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*	*Hrs. min.*
I	6 40	0.05	10 27	10 44	11 48	10 35	10 20	11 7	9 55	9 48	11 9	9 40	10 21
		0.10	7 7	13 28	21 7	7 57	7 32	7 39	7 16	12 36	20 39	7 40	7 50
		0.50	8 10	15 51	20 33	8 51	7 55	8 3	7 52	14 31	20 35	13 3	14 10
		1.00	7 54	56 19	29 5	7 15	8 16	8 2	8 1	9 15	49 40	7 5	7 15
II	5 44	0.05	9 39	10 29	9 31	8 39	9 10	9 18	9 3	11 2	12 2	10 8	10 3
		0.10	12 29	21 9	21 2	11 32	8 15	8 19	11 1	20 30	22 56	11 6	10 32
		0.50	8 33	13 2	16 11	8 14	8 13	6 6	8 5	19 28	22 13	7 57	8 0
		1.00	6 13	47 2	49 21	5 47	7 19	4 46	6 38	68 45	54 57	6 7	5 34
III	6 12	0.05	8 12	8 53	7 14	8 11	8 5	7 58	7 53	8 4	8 15	8 25	7 49
		0.10	8 30	15 2	14 4	8 10	8 28	8 26	13 58	10 50	14 39	7 58	7 59
		0.50	8 23	15 39	14 49	7 56	8 15	8 19	7 25	15 0	15 57	7 30	7 47
		1.00	8 41	50 58	15 58	8 47	6 48	6 30	5 36	34 39	20 57	4 12	6 34
IV	6 47	0.05	10 19	12 22	11 15	11 5	8 21	8 16	9 57	13 35	14 40	11 16	9 32
		0.10	8 51	13 57	14 19	8 45	11 12	10 14	11 25	13 28	14 50	10 29	10 29
		0.50	12 54	16 13	21 15	12 17	13 9	14 12	12 8	19 47	21 20	13 14	13 48
		1.00	7 56	51 38	60 19	7 2	8 3	9 10	7 45	54 42	82 47	5 33	6 18

DISCUSSION OF RESULTS

Tensile strength.—The general tendency of all the solutions is to decrease the tensile strength. Of the 352 results here recorded (which represent 1,056 briquettes), only 44 show an increase in strength, and as a rule, this increase is small. The greatest number of such cases occurs with the sulphates. The increases occur mostly with cements I and II and with the 1.0 and the 0.5 normal solution.

The decrease in tensile strength is most prominent with the 7-day briquettes, and the principal ones are with the maximum concentration of each solution employed. Cement IV is the most sensitive to the effect of the solutions in lowering the tensile strength. With this cement, every solution used causes one or more series of briquettes to fall below the specified limits. This cement is highest in calcium content.

Setting time.—Apparently there is no relation between the effect of the solutions on the set and on the tensile strength. On the basis of their effect on the set, the salts may be divided into two groups:

1. Sodium chloride, sodium nitrate, potassium nitrate, ammonium nitrate, sodium sulphate, sodium bicarbonate, and potassium bicarbonate.
2. Zinc chloride, copper chloride, zinc sulphate, and copper sulphate.

When a member of the first group is added to a cement, a small amount of the salt causes a retardation of the set. After a maximum point is reached, the set is accelerated by further additions of the substance, until the original setting time is reached or even passed. Within the limits investigated, the behavior of these electrolytes is, in general, similar to many others that have been investigated from time to time, such as sodium sulphide and calcium sulphate.[11] The second group shows a retardation with the lowest concentration of each solution employed. The retardation increases with increasing concentration. For the ranges studied the time-concentration curves of these salts rise indefinitely. This is contrary to the corresponding curves of group 1, which pass through maximum points.

Though it was expected that the results would tend to divide the salts into groups, the basis of division indicated by this work was somewhat surprising. This basis is not the solubility of the resulting calcium compounds nor the negative ion. It is chiefly the positive ion. Both zinc salts and both copper salts show similar effects, whereas the other chlorides and sulphates behave differently. Since calcium sulphate is difficultly soluble and calcium chloride is readily so, no division can be made on that basis. There are one or two exceptions to this effect of the zinc and copper compounds which are difficult to explain. These are the effect of copper chloride on sample III and the effect of zinc sulphate on sample I. However, in most cases all the cements are affected similarly by the same substances.

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[11] Witt, J. C., and Reyes, F. D., loc. cit.

A number of statements appear in the literature which attempt to account for the effect of electrolytes on cements, but usually there can be found as many exceptions as there are instances of agreement. For instance, Dobrzynski[13] found that the normal consistency of cement, when gauged with solutions of various chlorides, varied with the solubility of the salt. In the present work, cements gauged with sodium, copper, and zinc chlorides, which differ widely in solubility, showed the same normal consistency (Table IV). Kallauner is of the opinion that all soluble calcium salts decompose cement. This is not in conformity with other work with calcium salts (Table I). Though many believe that the major effect of an electrolyte is due to the effect of the negative ion, especially in so far as this may be able to affect the solubility of the calcium compounds in the cement, the present results do not indicate this. The statement of Rohland in various papers that cement is affected by catalizers positive and negative is not an adequate explanation. There are instances in which the great change in the setting time of cement caused by electrolytes seems to be catalytic, but in most cases the relation between the effect and the amount of the electrolyte present suggests some physical or chemical influence which is not catalysis but which has not as yet been explained.

SUMMARY

Investigation of the effect of certain substances on cement is becoming more important because of new industrial uses for concrete. The practical importance and the theoretical interest of the subject have led to the publication of a number of papers.

A study of these papers reveals that, while a number of them have individual merit, the results are not comparable and the subject as a whole shows little progress. One reason for this is that in carrying out investigations no definite plan of attack has been followed.

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[13] References are given in Table I.

Because of the complex nature of cements and the great difference in physical and chemical properties, it is believed that complete uniformity of results is not possible, but that qualitative agreement may be hoped for.

The general effect of all the electrolytes studied is to lessen the tensile strength and to modify the set.

On the basis of their effect on the set, the electrolytes may be divided into two groups. The members of one group cause a retardation of the set up to a certain concentration and then cause an acceleration. The members of the other group cause a retardation of the set which increases with the increase of the concentration, until the set is practically destroyed.

With the salts investigated in this paper the positive ion is more important than the negative in determining the effect of an electrolyte on cement. There is no well-established relationship between this effect and the solubility of any calcium compounds that may be formed. More extensive work will be necessary before the effect of an untried electrolyte can be predicated.

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